

IDENTIFICATION OF OXYGEN FUNCTIONAL GROUPS IN CARBONACEOUS MATERIALS USING OXYGEN K-EDGE XANES SPECTROSCOPY

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Introduction

The combustion of carbonaceous materials involves the formation of surface oxygen species. An understanding of the nature of these surface complexes is a necessary prerequisite for understanding the mechanism. Oxygen functional groups in carbonaceous materials can be determined by either selective chemical analysis techniques or spectroscopic methods. The former is limited by accessibility of the reagent to the carbon porous structure. A wide range of spectroscopic methods have been used *e.g.* Fourier transform infrared spectroscopy¹, nuclear magnetic resonance spectroscopy², X-ray photoelectron spectroscopy (XPS)^{3,4}, and Secondary-Ion Mass Spectrometry (SIMS)⁵. In spite of this, the current understanding of the structure, stability and reactions of the surface species is limited.

The aim of this study was to assess the potential of oxygen K-edge X-ray absorption Near Edge Structure (XANES) spectroscopy for the identification of oxygen functional groups in carbons and partially combusted carbons.

Experimental

Materials used. A series of organic compounds which contained specific oxygen functional groups were used as reference standards for the identification of the functional group peak energies.

A suite of partially-combusted chars were prepared by two methods: 1) combustion in a thermogravimetric analyser to a specific level of carbon conversion and 2) combustion in an entrained flow reactor for a specific residence time. The partially-combusted chars were stored under argon prior to the spectroscopic studies.

XANES Spectroscopy XANES measurements were carried out on beamline 1.1 of the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, UK. Beamline 1.1 uses a vertically-dispersing high energy spherical grating monochromator (HE SGM) to provide an X-ray source covering the energy range 250-1400 eV. This encompasses the 1s-electron (K edge) binding energies of carbon, nitrogen and oxygen. The

energy resolution at the oxygen K-edge (500-550 eV) was ~340 meV.

Samples were coated on 0.1 mm thick high purity (99.99%) platinum plates. The surface of the plates was roughened to ensure that the carbon particles adhered to the surface. A reference spectrum of a blank plate was recorded for each sample spectrum. The sample spectra were divided by the reference spectrum and the background subtracted. The XANES spectra are quoted on a relative energy basis⁶.

Results and Discussion

Figure 1 shows the oxygen K-edge XANES spectra of the oxygen functional group reference compounds over a 20 eV energy range. The spectra are reasonably sensitive to functional group type in terms of both the number of peaks and the peak energies. The spectra which show two peaks near to the absorption edge are those compounds which contain a C=O group. It is also apparent that lactones can be readily distinguished from anhydrides which is difficult using infrared spectroscopy.

The oxygen K-edge XANES spectra of acenaphthylene and partially combusted acenaphthylene chars are shown in Figure 2. The spectra of the partially combusted chars show the presence of bands which can be assigned to both carbonyl and carboxylic acid/acid anhydride functional groups.

The oxygen K-edge XANES spectra of Wearmouth coal chars produced in the EFR at 1250°C in pure nitrogen (35 ms) or an oxidising gas mixture (4% oxygen, balance helium) for residence times of 35 and 475 ms are shown in Figure 3. The spectrum of the char produced in pure nitrogen (35 ms residence time) is very similar to the spectra of phthalic anhydride and 1-naphthoic acid. This is consistent with Wearmouth being a high volatile bituminous coal. When the oxidising atmosphere is used, the spectrum shows the presence of a new peak which is consistent with the formation of carbonyl species. The XANES spectrum of the char produced with a residence time of 475 ms is very similar to the anthrone spectrum, although the peaks are less well resolved. The results clearly show

that the simultaneous loss of oxygen species originating in the coal and the formation of new surface complexes during combustion can be followed using this technique.

Conclusions

Oxygen K-edge XANES spectroscopy is a powerful technique for the identification of oxygen functional groups in carbonaceous materials. The results indicate that similar surface complexes are formed regardless of the nature of the carbonaceous material being combusted or the combustion temperature. Further work is required to confirm this by systematically varying combustion conditions over a wide range of temperature, carbon conversion level etc.

References

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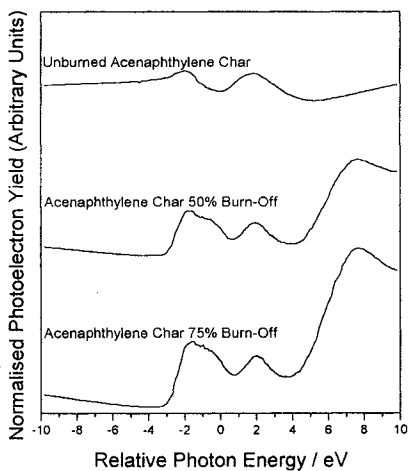


Figure 2. Oxygen K-edge XANES spectra of partially combusted acenaphthylene chars. Intensities not to scale.

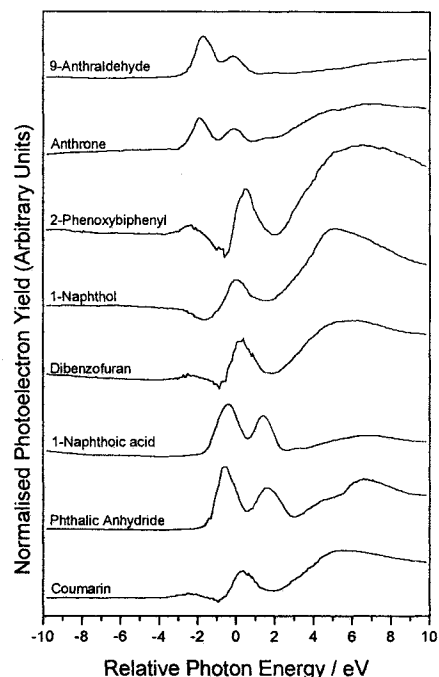


Figure 1. Oxygen K-edge XANES spectra of the functional group reference compounds. Intensities not to scale

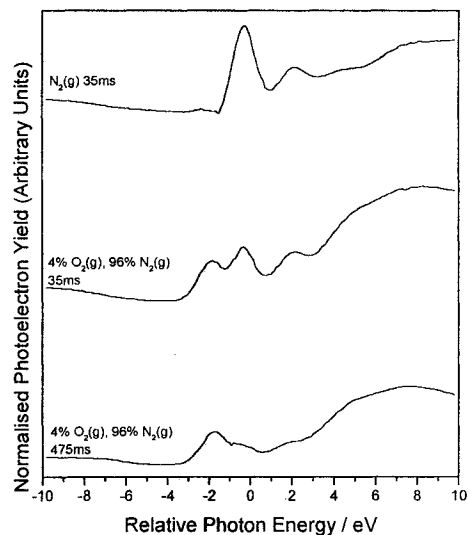


Figure 3. Oxygen K-edge XANES spectra of partially combusted Wearmouth coal chars. Intensities not to scale.